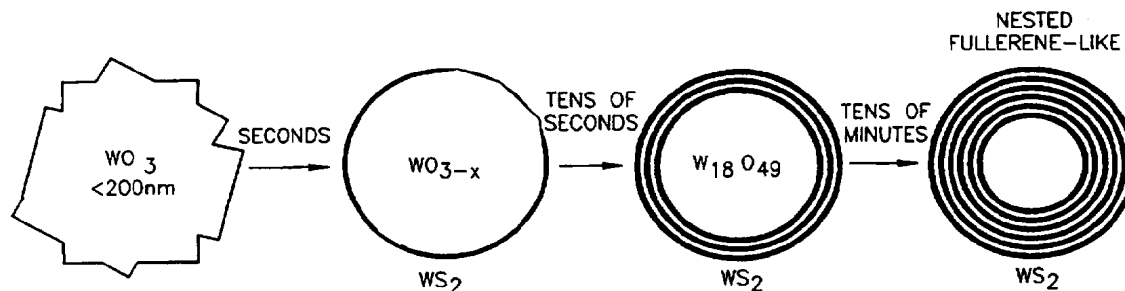




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C01G 1/12, 41/00, C01B 17/20, 19/00		A1	(11) International Publication Number: WO 97/44278
			(43) International Publication Date: 27 November 1997 (27.11.97)
(21) International Application Number: PCT/IL97/00165 (22) International Filing Date: 22 May 1997 (22.05.97) (30) Priority Data: 118378 22 May 1996 (22.05.96) IL (71) Applicant (for all designated States except US): YEDA RESEARCH AND DEVELOPMENT CO. LTD. [IL/IL]; Weizmann Institute of Science, P.O. Box 95, 76100 Rehovot (IL). (71) Applicants (for US only): MARGULIS, Helena (heiress of the deceased inventor) [IL/IL]; Ha'Irus Street 2/2, 70700 Gedera (IL). MARGULIS, Michael (heir of the deceased inventor) [IL/IL]; Leib Yaffe Street 7/25, 42490 Netanya (IL). MARGULIS, Maxim (heir of the deceased inventor) [IL/IL]; Ha'Irus Street 2/2, 70700 Gedera (IL). (72) Inventor: MARGULIS, Lev (deceased). (72) Inventors; and (75) Inventors/Applicants (for US only): TENNE, Reshef [IL/IL]; Hashomrim Street 21, 76231 Rehovot (IL). HODES, Gary [IL/IL]; Ganei Hadar 134, 73270 Gezer (IL). FELDMAN, Yishay [IL/IL]; Hapalmach Street 30, 77391 Ashdod (IL).		HOMYONFER, Moshe [IL/IL]; Dubnov Street 27, 58804 Holon (IL). (74) Agent: BEN-AMI, Paulina; Yeda Research and Development Co. Ltd., Weizmann Institute of Science, P.O. Box 95, 76100 Rehovot (IL). (81) Designated States: BR, CA, CN, IL, JP, KR, RU, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	

(54) Title: BULK SYNTHESIS OF INORGANIC FULLERENE-LIKE STRUCTURES OF METAL CHALCOGENIDES



(57) Abstract

A method and apparatus for preparing inorganic fullerene-like nanoparticles of a metal, e.g. transition metal, chalcogenide having a desired size and shape in high yields and macroscopic quantities, the method comprising the steps of (a) dispersing solid particles of at least one non-volatile metal material having the preselected size and shape; (b) heating the solid particles of the non-volatile metal material in a reducing gaseous atmosphere containing at least one chalcogen material for a time and a temperature sufficient to allow the metal material precursor and the chalcogen material to react and form at least one layer of metal chalcogenide, the at least one layer of metal chalcogenide encasing the surface of the solid particles to form the fullerene-like particles; and (c) recovering the thus obtained macroscopic quantities of the IF-metal chalcogenide of the desired size and shape.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

5 BULK SYNTHESIS OF INORGANIC FULLERENE-LIKE STRUCTURES OF
METAL CHALCOGENIDES

FIELD AND BACKGROUND OF THE INVENTION

10 The present invention relates in general to a method and apparatus for
preparing inorganic fullerene-like structures of metal, e.g. transition metal,
chalcogenides, and more particularly, to a solid-gas method and reactor for high
yield preparation of macroscopic quantities of such inorganic fullerene-like particles
of desired size and shape.

15 Graphite is the most stable form of carbon under ambient conditions.
Nevertheless, graphite nanoclusters have been shown to be unstable against folding
and close into fullerenes (Kroto et al., 1985), nested fullerenes (Iijima, 1980) and
nanotubes (Iijima, 1991). It is believed (Robertson et al., 1992) that the main
stimulus to form carbon fullerenes (CF) emanates from the large energy associated
with the dangling covalent bonds of the peripheral carbon atoms in graphite
20 nanoclusters.

Notwithstanding the efforts to develop synthetic routes for mass production of
carbon fullerenes, nested fullerenes ("buckeyonions"), nanotubes, etc., the generic
technique for the synthesis of such phases remains arc-discharge (Kratschmer et al.,
1990; Ebbesen and Ajayan 1992) and subsequent extraction from the soot.

25 A similar process is also used for the synthesis of BN or $B_xC_yN_x$ nanotubes
(Stephane et al., 1994; Weng-Sieh et al., 1994), metallocarbohedrenes (Met-Cars)
(Cartier et al., 1995), endohedral fullerenes (Chai et al., 1991; Takata et al., 1995) and
nanotubes (Ruoff et al., 1993; Seraphin et al., 1993). Obviously, this method is
neither very easy to control nor amenable to an easy scale-up. The ensuing
30 purification processes are tedious and time consuming, which influences the cost of
the final product.

Key steps in the growth mechanism of the above products were elucidated (Jarrold et al., 1994), but the detailed mechanism of the reaction is still a matter of controversy.

Therefore, the size distribution of nanotubes and nested fullerenes cannot be adequately controlled and is relatively wide. For both structural species, the innermost layer serves as a template for the growth of the top layers, which usually grow outwards (Ugarte, 1992), possibly in an accretion (snail-like) growth mode (Kroto, 1988).

Particles of inorganic structures having a layered configuration (a single layer or nested layers) are known as inorganic fullerenes (IF). For ease of discussion, inorganic layered structures such as but not limited to spheres, whiskers, nanotubes, polyhedral and others, will interchangeably be referred to as "inorganic fullerene-like" or "IF" materials, throughout the specification.

Nanoclusters of IF metal chalcogenide materials, such as WS₂ and MoS₂, were recently described (Tenne et al., 1992; Margulis et al., 1993; Hershfinkel et al., 1994; EP 0 580 019). Thus, according to published European Patent Application No. O 580 019 of the same applicants, a method was described for the preparation of oriented thin films of the transition metal chalcogenides WS₂, WSe₂, MoS₂ and MoSe₂ from the corresponding metal oxides, whereby in some conditions the nanoclusters of the layered IF metal chalcogenide materials were shown to be unstable against folding and to close upon themselves to form nested IF nanoparticles such as nested fullerene-like structures and nanotubes. These conditions could not be controlled and thus the method according to the above-mentioned publications do not allow to obtain high yields of macroscopic quantities of the IF metal chalcogenide, nor to determine the size and shape of the particles.

A gas phase synthesis for the preparation a few milligrams of IF-MoS₂ from a molybdenum trioxide precursor and H₂S in a reducing atmosphere has been described (Feldman et al., 1995; Srolovitz et al., 1995), taking advantage of the sublimation of the molybdenum suboxide (MoO_{3-x}) under reducing conditions

above 700 °C. Thus, a portion of 30 mg of MoO₃ powder (>99% pure) was heated (>800 °C) and slowly reduced to MoO_{3-x} by a stream of forming gas (typically 5%H₂/95%N₂). The suboxide (MoO_{3-x}) sublimed and effused out of a nozzle where it crossed a stream of H₂S gas mixed with a forming gas. After some 3-5 minutes, the entire load (30 mg) of MoO₃ sublimed, the reaction products were collected on a quartz substrate, positioned few cm away from the crossing point of the two gas streams and maintained at the same temperature (>800 °C), and the collected nanoparticles were progressively converted into nested layer polyhedra within ca. 30 minutes of firing time. The average size of the oxide particles and the ensuing IF-MoS₂ particles increased with temperature. It was found that above 900 °C, platelets with 2H-MoS₂ structure abound, and became the sole product above 950 °C. According to the above-described gas phase reaction it is not possible to obtain very high quantities of the IF structures of transition metal chalcogenides nor to select in advance their size and shape. It is difficult to modify or to control the shape of the molybdenum oxide precursor since sublimation is involved.

The IF particles have several interesting and useful applications, and it would be very advantageous to have a method and apparatus for high yield preparation of macroscopic quantities of IF particles of metal, e.g. transition metal, chalcogenides having a desired size and shape.

SUMMARY OF THE INVENTION

It has now been found according to the present invention that it is possible to prepare macroscopic quantities of IF structures of metal chalcogenides having a desired size and shape by selecting a solid non-volatile metal material precursor having said desired size and shape and carrying out the reaction of the solid metal material particles in the nanometer range with a chalcogen material in a reducing gaseous atmosphere while controlling time and temperature. The size and shape of the thus produced IF particles are determined by the size and shape of the incipient

metal material precursor, and thus the preselection of the precursor material leads to the IF structures of the desired size and shape.

It should be noted that the term "inorganic fullerene-like" ("IF"), as used herein in the specification and claims, refers to inorganic metal chalcogenide structures having one layer or nested layers which form what is known in the art as a closed cage (Tenne et al., 1992; Margulis et al., 1993) which may encage a void (i.e., be hollowed) or a core or may form a stuffed nested layer structure, i.e. a structure containing a material other than the metal material precursor encaged within nested layers of the metal chalcogenide. In particular the term refers to structures such as what is known in the art as single and double layer inorganic fullerenes (Srolovitz et al., 1995), nested layers inorganic fullerenes (Tenne et al., 1992), stuffed inorganic fullerenes (Margulis et al., 1993, single layer nanotubes (Bethune et al., 1993; Iijima and Ichiashi, 1993), nested nanotubes (Iijima, 1991) stuffed nanotubes (Ajayan and S. Iijima, 1993), and inorganic superlattice structures, i.e. IF particles having layers of two or more different chalcogenides of the metal, e.g. WS_2 and WSe_2 .

According to the method and apparatus of the present invention, IF nanoparticles of metal chalcogenides including one or more layers of desired sizes and shapes, e.g., spheres, sphere-like, nanotubes and polyhedral shapes, may be manufactured.

The metals that are suitable for this method are metals that form layered metal chalcogenide products in a solid-gas reaction such as In, Ga, Sn and a transition metal selected from Mo, W, V, Zr, Hf, Pt, Re, Nb, Ta, Ti, Cr and Ru.

The present invention thus relates in one aspect to a solid-gas method for the bulk synthesis of inorganic fullerene-like (IF) structures of metal chalcogenides from a solid non-volatile metal material precursor, said IF structures having a desired size and shape being predetermined by the size and shape of the said metal material precursor, wherein said metal is selected from In, Ga, Sn and a transition metal selected from Mo, W, V, Zr, Hf, Pt, Re, Nb, Ta, Ti, Cr and Ru, said method comprising the steps of:

(a) dispersing in a reactor solid nanoparticles of at least one non-volatile metal material having the preselected size and shape, said dispersion being such that, upon heating, agglomeration and fusion of said solid nanoparticles into larger particles are substantially avoided, while the top surface of said solid particles is substantially completely exposed to a gaseous atmosphere;

(b) heating said dispersed solid particles of said metal material in a reducing gaseous atmosphere containing at least one chalcogen material for a time and a temperature sufficient to allow the reaction of the top surface of said metal material nanoparticles with said chalcogen material gas, thus obtaining IF nanoparticles of the desired size and shape, said IF nanoparticles having at least one completely closed monomolecular metal chalcogenide layer encaging said metal material particles; and

(c) recovering the thus obtained macroscopic quantities of the IF structures of the desired size and shape.

Heating in step (a) is carried out at a temperature within the range of 650-850 °C for a time shorter than 60 seconds to produce IF structures with one layer encaging said metal material, and for 1-20 min to produce IF structures with 2-5 layers encaging said metal material.

In another aspect, the method of the present invention comprises further heating at the same temperature the IF particles of step (a) in said reducing gaseous atmosphere containing said at least one chalcogen material gas, for a time sufficient to allow said metal material and said chalcogen material gas to further react through a slow diffusion controlled reaction, wherein the metal material core is progressively converted into a metal chalcogenide nanoparticle with an empty core, and nested IF structures are thus obtained and recovered.

In this aspect of the invention, the reaction mixture is further heated at 650-850 °C for 20-120 min to produce multilayered IF structures. The heating time is shorter for the production of metal sulfides and longer for the corresponding metal selenides. For example, for the production of small particles (ca. 20 nm) of metal

sulfides, the metal material precursor should be heated with H_2S for less than 60 min, while for the production of larger particles (>50 nm), the heating time should be 90-120 min.

In all steps, heating above 900°C , as described in the prior art methods mentioned above, should be avoided, since it leads to production of platelets of metal chalcogenides, e.g. 2H-WS_2 platelets, and not to IF-WS_2 structures.

Examples of metal chalcogenides that form layered products and are suitable for the preparation of IF structures according to the method of the invention include, but are not limited to, WS_2 , WSe_2 , MoS_2 , MoSe_2 , SnS_2 , SnSe_2 , RuS_2 , GaS , GaSe , In_2S_3 , In_2Se_3 , InS , InSe , etc. (for additional examples, see A. F. Wells, *Structural Inorganic Chemistry*, 5th edition, Oxford Science Publications (1993); *Chemistry of the Elements*, by N. N. Greenwood and A. Earnshaw, Pergamon Press, Oxford (1990)).

In a preferred embodiment of the method of the invention the metal is a transition metal. selected from Mo, W, V, Zr, Hf, Pt, Re, Nb, Ta, Ti, Cr and Ru.

The metal, preferably transition metal, material used as precursor in the method of the invention is at least one non-volatile metal material selected from the group consisting of a metal, a compound containing a metal, a mixture of metals, a mixture of compounds containing a metal and a mixture of a metal and a compound containing a metal. Examples of such metal materials are non-volatile metals, mixtures of metals, alloys e.g. $\text{W}_{0.2}\text{Mo}_{0.8}$, metal oxides and metal carbides.

In one preferred embodiment the metal material is a metal oxide selected from a tungsten oxide selected from WO_3 , $\text{W}_{20}\text{O}_{58}$, and $\text{W}_{18}\text{O}_{49}$; ZrO_2 , HfO_2 , PtO_2 , In_2O_3 , Ga_2O_3 , Nb_2O_5 , Ta_2O_3 , ReO_3 , TiO_2 , SnO_2 , and RuO_2 .

The chalcogen according to the invention is S, Se or Te, and the chalcogen material as defined herein is selected from the group consisting of a chalcogen, a compound containing a chalcogen, a mixture of chalcogens, a mixture of compounds containing a chalcogen and a mixture of a chalcogen and a compound containing a

chalcogen. The chalcogen material is preferably a chalcogen compound containing hydrogen, more preferably H_2S , H_2Se , and/or H_2Te .

The size of the IF particles produced by the method of the invention is selected according to the potential application of the IF structures and is in the nanometer range, preferably <300 nm, more preferably <150 nm, and most preferably <30 nm.

The shape of the IF nanoparticles produced by the method of the invention is also selected according to the potential application of the IF structures and is determined by the shape of the metal material precursor. Thus sphere-like particles and whiskers of the metal material precursor will produce sphere-like particles and nanotubes, respectively, of the metal chalcogenides.

The IF structures produced by the method of the invention include, but are not limited to, single layer inorganic fullerenes, nested layers inorganic fullerenes, stuffed inorganic fullerenes, single layer nanotubes, nested nanotubes, stuffed nanotubes, inorganic supperlattice structures, and structures with negative curvature (Schwartzites).

It is possible according to the method of the invention to predetermine the number of layers of the end product by controlling the time of reaction. Thus sphere-like particles and nanotubes having a metal material core encaged within 1-5, preferably 2-3, layers of the metal chalcogenide are suitable for use as battery cathodes, while multilayered partially and fully transformed IF nanoparticles are suitable for solid lubrication, and fully transformed IF nanoparticles are suitable for photocatalysis.

In one preferred embodiment of the method of the invention, the metal material is WO_3 and the chalcogen material is H_2S gas. The solid WO_3 nanoparticles are first dispersed on the floor of the reactor to avoid agglomeration and fusion of the heated nanoparticles, the dispersed nanoparticles of WO_3 are reacted at a temperature in the range of 650 - 850°C with a mixture of H_2S gas with a forming gas, typically 5% H_2 /95% N_2 , whereby the WO_3 is reduced to WO_{3-x} and gradually converted to

WS₂, and the reaction products are collected on a substrate and progressively converted into the desired nested IF-WS₂ polyhedra.

In another aspect, the invention relates to an apparatus for preparing macroscopic quantities of inorganic fullerene-like nanoparticles of metal chalcogenides having a desired size and shape according to the method of the invention, the apparatus comprising:

(a) a bundle of small tubes [12] arranged within a main tube [14], each of said small tubes being for accommodating a preselected quantity of solid nanoparticles of at least one non-volatile metal material having the preselected size and shape;

(b) a gas flux inlet in said main tube for introducing a forming gas and at least one chalcogen material gas; and

(c) heating means for heating said small tubes;

said preselected quantity of the metal material being selected such that said solid nanoparticles are dispersed to a degree such that agglomeration and fusion of said solid nanoparticles into larger particles during said heating are substantially avoided, while the surface of said nanoparticles is substantially completely exposed to said chalcogen material gas.

Said apparatus may further comprise: (d) first flow control means for controlling the flow of forming gas; and (e) second flow control means for controlling the flow of chalcogen material gas.

In still another aspect, the present invention relates to an apparatus for preparing macroscopic quantities of inorganic fullerene-like nanoparticles of metal chalcogenides having a desired size and shape according to the method of the invention, the apparatus comprising:

(a) a chamber having a lower end and an upper end, said chamber being for accommodating solid nanoparticles of at least one non-volatile metal material having a preselected size and shape;

(b) a gas penetrateable cover covering said lower end of said chamber, said gas penetrateable cover being for providing said chamber with an inward flow of carrier gas for floating said solid particles in said chamber;

(c) a gas outlet located at said upper end of said chamber for sustaining said flow of gas;

(d) first means for introducing said solid particles into said chamber;

(e) second means for introducing at least one chalcogen material into said chamber; and

(f) heating means for heating said chamber;

said flow of gas being selected such that said solid nanoparticles of the metal material are dispersed to a degree such that agglomeration and fusion of said solid particles into larger particles during said heating are substantially avoided, while the surface of said solid particles

5 The method and apparatus described above allow the preparation of inorganic fullerene-like materials of metal chalcogenides having preselected size and shape in high yields and macroscopic quantities.

Several applications have been proposed for semiconducting transition metal chalcogenides, e.g., WS₂, WSe₂, MoS₂, MoSe₂, SnS₂, SnSe₂, RuS₂, GaS, GaSe, 10 InS, InSe, etc., including electrochemical and photovoltaic solar cells production (Abruna and Bard 1982; Djemal et al., 1981); photocatalysis (Rosenberg et al., 1992; Dagan and Tomkiewicz, 1993); and in solid lubrication, such as in high or low temperature environments or under ultra high vacuum where liquid lubricants are not suitable (Dimigen et al., 1979), and in ferrofluid lubrication, sealing and levitation 15 applications.

IF materials of the above mentioned compounds are believed to outperform the bulk materials in the aforementioned applications. Since the outer surface of the IF material exposes only the basal plane of the compound, this material lends itself to solid lubrication applications. Indeed, IF nanoparticles do not stick to each other or 20 the substrate and exhibit poor surface adhesion. Their approximate sphero-symmetric

shapes imply easy sliding and rolling of the nanoparticles and consequently very small shear forces are required to move them on the substrate surface. The absence of edges in IF semiconductors is believed to alleviate the problem of surface recombination which hinders the application efficiency of the bulk photocatalysts.

5 Other possible applications involve battery cathodes (Rouxel and Brec, 1986), and catalysis (Chianelli, 1984). In addition, accumulating evidence indicate that such IF particles may be used in the field of nanoelectronics and magnetic information storage, since such particles exhibit magnetic phase transition. It will be appreciated by one ordinarily skilled in the art that for many such applications the ability to
10 preselect the size and shape of the IF particles is of great importance. This is the case when solid lubrication is of concern since controlling the size and shape determines the surface energy of the particles which is of great importance concerning lubrication capabilities. This is also the case when photocatalytic and photovoltaic capabilities are of concern, since the size and shape of the particles determine the
15 absorption spectrum and the lifetime of excited carriers which are responsible for photocatalytic and photovoltaic functions, respectively. The high precision characterizing the field of nanoelectronics and magnetic information storage also requires precision in size and shape of the IF particles.

20 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic representation of the growth model of the inorganic fullerene-like phase of IF-WS₂ nested polyhedra from oxide nanoparticles according to the method of the present invention.

25 Figs. 2A-2C are transmission electron microscopy (TEM) micrographs showing the gradual transformation of tungsten oxide nanoparticles into IF-WS₂ nested polyhedra, according to the method of the present invention.

Figs. 3A-3D are TEM micrographs showing the transformation of tungsten oxide nanoparticles into IF-WS₂ according to the method of the present invention, wherein Fig. 3A shows a typical assortment of tungsten oxide particles with <10 nm

diameter which are transformed into IF-WS₂ particles of a similar size and shape, shown in Fig. 3B, whereas Figs. 3C and 3D show a similar transformation for tungsten oxide particles with a diameter in the range of 50-150 nm.

Fig. 4 shows the transformation of WO₃ nanoparticles into IF-WS₂ followed by X-ray powder diffraction, wherein curve A presents diffraction of the WO₃ precursor powder, curve B presents the same powder after two minutes of HS₂ annealing, curve C presents the powder after eight minutes annealing, curve D presents the powder after fifteen minutes annealing and curve E presents the powder after 120 minutes annealing, wherein the annealing conditions are: 850 °C, rates of gas flow: forming gas, 130 cc/min; H₂S gas -- 2 cc/min.

Fig. 5 depicts optical absorption measurements of composite IF-WS₂/WO_{3-x} sample after 3 min annealing (dashed line) and after 120 min annealing (solid line). The annealing conditions are as in Fig. 4 above.

Fig. 6 is a cross section view of an apparatus used for high yield synthesis of macroscopic quantities of transition metal chalcogenides according to the present invention.

Fig. 7 is a cross section view of an apparatus used for high yield synthesis of macroscopic quantities of IF-WS₂ particles in a solid-gas continuous process according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is directed to a method and apparatus for high yield preparation of macroscopic quantities of inorganic fullerene-like (IF) nanoparticles, i.e., particles in the nanometer range, of In, Ga, Sn and transition metal chalcogenides, wherein the transition metal is Mo, W, V, Zr, Hf, Pt, Re, Nb, Ta, Ti, Cr or Ru, which IF structures can be used for production of electrochemical and photovoltaic solar cells, solid lubrication, photocatalysis, production of battery cathodes, catalysis and numerous other applications.

A schematic representation of the growth model of WS₂ particles according

to the method of the invention is depicted in Figure 1. Within the first few seconds of the reaction, the top surface of the sublimed oxide nanoparticle reacts with H_2S gas and a completely closed monomolecular WS_2 layer or two are formed. The inert surface-sulfide layer, prohibits fusion of nanoparticles into macroscopic entities, which would lead to the formation of e.g., a 2H- WS_2 phase. Fast hydrogen diffusion into the nanoparticle leads to a complete reduction of the oxide core into $\text{W}_{18}\text{O}_{49}$ within a minute or two (Kung, 1989). Subsequently, the oxide core is progressively converted into WS_2 through a slow diffusion-controlled reaction, which ends after ca. 60 minutes. Consequently, the size and shape of the IF particle thus formed is determined by the size and shape of the incipient oxide nanoparticle.

It will be appreciated by one ordinarily skilled in the art that the above described growth mechanism of metal chalcogenide IF particles is very much different from other growth mechanisms attributed for other types of particles growing outwardly possibly in an accretion (snail-like) growth mode (Iijima and Ichiashi, 1993; Ugarte, 1992; Kroto, 1988), as being an inwards type growth mechanism; and therefore the size and shape of the products (i.e., IF particles) may be determined by selecting the size and shape of the reactants. The above described growth mechanism differs also from the growth mechanism of platelets with e.g., two repeat units and hexagonal packing (2H), or three repeat units with rhombohedral packing (3R), etc., (Wilson and Yoffe, 1968).

As mentioned above and is briefly repeated here, the gas-phase reaction previously disclosed (Feldman et al., 1995; Srolovitz et al., 1995) has major limitations rendering it not suitable for the production of macroscopic amounts of IF particles of metal chalcogenides having preselected size and shape. These limitations include (a) a requirement for a careful control over the growth conditions such as temperature, reactants concentration, etc.; (b) requirements for a specific geometry of the reactor and a specific turbulent flow regime; (c) the size of such gas-phase formed structures is highly subjective to reaction conditions, especially gas flow and turbulence, and reaction temperature; (d) a fairly large distribution in size

of the structures formed is experienced, whereas the shape is spherical in nature, thus, the size and shape of the structures thus produced cannot be tailored according to specific needs; (e) since a careful control of reaction parameters is of great importance, scaling-up the process to obtain commercial macroscopic quantities of IF particles is highly limited; and (f) yields are typically low even under the best of reaction conditions (e.g., ranging between 5% and 20%).

The method of the present invention provides bulk synthesis, i.e. high yield preparation of macroscopic quantities of inorganic fullerene-like (IF) particles of metal chalcogenides having a preselected size and shape, and includes (a) dispersing solid particles (e.g., a powder) of at least one non-volatile metal material precursor having the preselected size and shape; and (b) heating the solid particles of the metal material in a gaseous reducing atmosphere containing at least one chalcogen material for a time and a temperature sufficient to allow the metal material(s) and the chalcogen material(s) to react and form at least one layer (typically one or two layers at this early stage) of metal chalcogenide, which is encaging (i.e., engulfing) the surface of the solid precursor particles to form the IF particles.

A most important feature of the method of the present invention is that the dispersion of the solid particles is such that agglomeration and fusion of the solid particles into larger particles upon heating are substantially avoided (i.e., preferably at least 90%, more preferably 95%, most preferably 99% or more percent of the solid particles are in no contact with neighboring particles), so that the surface of the solid particles is substantially completely (i.e., preferably 90% of which, more preferably 95% of which, most preferably 99% or more percent of which) exposed to the gaseous atmosphere.

The required dispersion of the solid particles according to the present invention may be achieved in one of many alternatives. For example, agitating (e.g., by ultrasonic agitation) the tube or vessel in which the reaction takes place ensures the required dispersion. Alternatively, performing a fluidized bed process in which the flow of gaseous atmosphere containing the chalcogen material(s) floats the

particles during the reaction may account for proper dispersion of the solid particles (further details concerning the fluidized bed process may be found in Perry's Chemical Engineers Handbook, 1984).

The method of preparing IF particles according to the present invention is by
5 a solid-gas phase reaction and is therefore less dependent upon reaction conditions such as gas flow and turbulence regimes, etc. as compared with the known gas-phase reaction. Furthermore, as is described in greater detailed herein below, yields of such solid gas phase reactions are exceptionally high, in many cases reaching substantially 100%, and the amount of product (i.e., IF particles) obtained is
10 substantially unlimited since scaling-up such reactions, as opposed to gas-phase reactions, is fairly feasible, leading to the formation of macroscopic quantities of product.

Depending on the number of nested layers required from the product, step (b) of the method according to the present invention may be continued for a time and a
15 temperature sufficient to allow the metal material and the chalcogen material to further react and form nested layers of metal chalcogenide. The number of layers obtained using the method of the present invention is fairly unified since all particles are exposed to the same reaction conditions for a predetermined time period. This is however not the case using the prior art gas-phase reaction described hereinabove,
20 since different particles sublime at different times after reaction starts.

It is also encompassed by the present invention the preparation of superlattice IF particles, which are particles having layers of at least a first type and a second type metal chalcogenide (e.g., WS_2 and WSe_2 , respectively), whereby a metal material, say WO_3 , is reacted with a first chalcogenide material, say H_2S , and
25 the product of this reaction is thereafter reacted with a second chalcogenide material, say H_2Se . In this case, the outer layers of the resulting superlattice IF particles would be of the first type metal chalcogenide, whereas the inner layers would be of the second metal chalcogenide. Similarly, superlattices having layers of additional

types of metal chalcogenide (e.g., WTe_2) or alternating layers (e.g., WS_2 , WSe_2 , WS_2 , WSe_2 , etc.) or any other layer arrangement, may be produced.

Since, as explained in greater details below, once a first layer of metal chalcogenide encages the solid particles they can no longer fuse and form agglomerates, the method according to the present invention preferably includes a step in which the IF particles having one or two encaging layers of metal chalcogenides as described above are collected into a dense arrangement prior to continuing the reaction as described to obtain particles of nested layers. Thus, in an embodiment highly suitable for commercial mass production of IF particles, the solid particles are first reacted such that they are covered by one or two layers of metal chalcogenide, the particles are then collected into a smaller volume (i.e., dense arrangement) and the reaction is continued until a desired number of nested layers encage the particles.

Since by selecting the size and shape of the solid metal material precursor particles one is determining the size and shape of the IF-metal chalcogenide particles formed, a careful selection of sizes and shapes of the precursor particles is used according to the method of the present invention to tailor IF particles of various selected sized and shapes such as but not limited to spheres, sphere-like and nanotubes, according to any specific needs or requirements.

The size of the solid precursor particles and the reaction temperature with the chalcogen material gas are of great importance for the formation of the IF particles as opposed to other shapeless and amorphous products (e.g., platelets). Therefore, the size of the solid particles is in the nanometer range, i.e. less than 300 nm, preferably less than 150 nm, most preferably less than 30 nm in, for example, diameter, and the reaction temperatures are typically maintained below 850 °C, depending on particle size.

The solid-gas reaction of the present invention may be carried out in a closed system containing the dispersed solid metal material particles and the chalcogen material reducing gaseous atmosphere, yet in a preferred embodiment of the

invention, the reaction is carried out in an open system and the gaseous atmosphere is supplied in the form of a gas flow. This architecture of the system ensures that the surface of each of the particles is constantly in contact with identical concentrations of the chalcogen material(s) in the gaseous atmosphere. The open system may thus include an open tube in which the solid particles are dispersed and means to ensure flow of the described gaseous atmosphere. Since, as is described in further detail hereinbelow, the reactions are typically performed under relatively high temperatures, the tube is preferably made of a heat resisting and chemically inert substance such as but not limited to quartz or a ceramic material, e.g., alumina, sapphire, zirconia, silicon carbide, tungsten carbide, etc.

The principles and operation of a method and product according to the present invention may be better understood with reference to the examples and descriptions below, including the accompanying drawings. A number of examples are given to illustrate various aspects of the present invention. The discussion which follows concentrates on the WS_2 system, it being understood that this discussion is illustrative only and is not intended to limit the scope of the present invention to that system.

EXAMPLE 1

A solid (WO_3)-gas (H_2S+H_2) reaction was carried out for the synthesis of sphere-like IF particles of WS_2 . Thus 100 mg of sphere-like WO_3 powder (>99% pure) nanoparticles with particle sizes smaller than ca. 30 nm were carefully dispersed on the entire floor of a quartz tube reactor to avoid agglomeration and fusion of the heated nanoparticles, resulting in a substantial complete exposure of the nanoparticle surface to the reacting gas. The reactor was inserted into an oven heated to 750 °C, in which a constant flow of forming gas (95% N_2 / 5% H_2 ; 110 cc/min) and H_2S (2 cc/min) was provided. Portions of the powder were retracted from the oven at different times and examined by transmission electron microscopy (TEM). The micrographs are shown in Figs. 2A-2C, wherein Fig. 2A shows the IF-

WS₂ nanoparticles recovered after 1 min, Fig. 2B after 10 min, and Fig. 2C after 30 min.

It is to be noted that non-desired 2H-WS₂ platelets were predominantly obtained under the following experimental conditions: (a) packing of the powder was too compact; (b) oxide precursor particles with sizes above 0.2 μm were used; and/or
5 (c) reaction temperature exceeded 900 °C.

EXAMPLE 2

500 mg of sphere-like WO₃ powder (>99% pure) nanoparticles having
10 particle size < ca. 20 nm (shown in Fig. 3A) were carefully spreaded in a quartz tube reactor according to Fig. 6 herein, and sulfidized by heating the oven to 700 °C under a constant flow of forming gas (95% N₂ / 5% H₂ ; 200 cc/min) and H₂ S (8 cc/min). The synthesis was stopped after 30 min and the IF-WS₂ nanoparticles were recovered and examined by TEM. The micrograph depicted in Fig. 3B shows that the
15 IF-WS₂ particles of Fig. 3B are evidently close in size and shape to the oxide particles of Fig. 3A.

EXAMPLE 3

500 mg of sphere-like WO₃ powder (>99% pure) nanoparticles having
20 particle size < ca. 50-150 nm (shown in Fig. 3C) were loosely dispersed in a reactor according to Fig. 6 herein, and the reactor was inserted into an oven heated to 830 °C under a constant flow of forming gas (95% N₂ / 5% H₂ ; 200 cc/min) and H₂S (8 cc/min). After 90 min the black powder was retracted from the oven and examined by TEM. IF-WS₂ nanoparticles (Fig. 3D) of a similar size and shape to the oxide
25 precursor nanoparticles (Fig. 3C) were obtained.

It should be noted that in the conditions of Examples 1-3, the H₂S gas reacts uniformly with all oxide particles in the powder, and hence the number of sulfide layers is essentially the same for all intermediate IF-WS₂/oxide composite nanoparticles obtained.

Since the outer surface of the IF-WS₂ layered material exposes only the basal plane of the compound, this material lends itself to solid lubrication applications. Indeed, IF nanoparticles do not stick to each other or the substrate and exhibit poor surface adhesion. Their approximate sphero-symmetric shapes imply easy sliding and rolling of the nanoparticles and consequently very small shear forces are required to move them on the substrate surface. The oxide core provides the necessary mechanical toughness to the IF particles. Further, the potential of inorganic transition metal IF particles for photocatalysis is promising due to the strong optical absorption, large surface area and the documented chemical inertness under illumination (Tributsch, 1982).

Complementary information on the reaction mechanism was obtained by using a combination of the following techniques: (a) transmission electron microscopy (TEM); (b) electron diffraction (ED); (c) X-ray powder diffraction (XRD); (d) X-ray photoelectron spectroscopy (XPS), and (e) optical absorption measurements.

EXAMPLE 4

100 mg of WO₃ powder (ca. 100 nm) were H₂S annealed in a quartz tube reactor at 850 °C under a constant flow of forming gas (95% N₂ / 5% H₂ ; 130 cc/min) and H₂S (2 cc/min). Portions of the powder were taken for X-ray diffraction (XRD) measurements after various periods of time.

XRD spectra of powder samples acquired during different stages of the annealing process of WO₃ with H₂S are shown in Fig. 4. Curve A shows the XRD pattern of the WO₃ precursor. As shown in curve B, after 2 minutes of annealing, a small WS₂ peak is observed. Astonishingly, the entire nanoparticle core has been reduced to W₁₈O₄₉, at this early stage of the process. This fact can be understood assuming that hydrogen and water diffuse appreciably faster than sulfur diffuses to form sulfide. Curve C shows the state of the sample after 8 minutes annealing, while curve D displays the XRD pattern of the sample after 15 minutes annealing time.

The XDR of the fully converted sample (120 minutes annealing time) is shown in curve E. The shift of the (0002) peak of the IF-WS₂ phase (curves A-E) indicates a lattice expansion of ca. 2% between two adjacent WS₂ slabs along the c-axis, which is attributed to the strain in the bent layers (Feldman, 1995). Furthermore, since the number of atoms in the layer increases with its radius, the layers cannot be fully commensurate. This discrepancy can be partially alleviated by lattice expansion along the c-axis.

EXAMPLE 5

The preparation of IF-WS₂ was carried out as in Example 4. With reference now to Fig. 5, the transformation of WO_{3-x} into IF-WS₂, was further followed by optical absorption spectra using stirred alcoholic suspensions of samples drawn after 6 minutes and 120 minutes annealing time, as measured at room temperature. The oxide absorption peak of the composite oxide/sulfide (6 minutes annealing time) could be easily resolved in the difference spectrum and is substantially redshifted, compared to the literature value (Porter et al., 1969). Remarkably, IF-WS₂ powder consisting of particles smaller than 10 nm, formed a stable alcoholic colloid exhibiting a strong blue shift of the excitonic absorption, which could be possibly assigned to a quantum size effect.

EXAMPLE 6

The preparation of IF-WS₂ was carried out as in Example 4. Being a surface sensitive technique, X-ray photoelectron spectroscopy (XPS) could be ideally suited for investigating the sulfide/oxide superstructure. Accordingly, few mg of IF-WS₂ powder were pressed onto an indium plate, which provided the support and electrical contact for the powder. A sequence of four samples consisting of composite nanoparticles of IF-WS₂ (shell)/tungsten oxide (core) at different annealing times were investigated: Sample 1 -- 2 minutes; sample 2 -- 6 minutes; sample 3 -- 15

minutes; and sample 4 -- 2 hr annealing time. In addition, reference WS₂ crystal, WO₃ powder and a clean indium specimen were measured.

The fraction of oxide particle converted into sulfide was determined in two independent ways, which gave similar results. First, the concentration of the two compounds was determined from the analysis of the total concentrations of the various elements, and second, from the tungsten 4f-5p spectral region which was deconvoluted into sulfide (4f_{7/2}=32.6; 4f_{5/2}=34.75; 5p_{3/2}= 38.3 eV) and oxide (shifted to higher energies by 3.0 eV). Shirley background subtraction was used for spectra analysis (Briggs and Seah, 1990).

While the indium contribution to the total signal was less than 1%, carbon made up to 18% of the total material. Yet, by comparing the tungsten and sulfur lineshapes with those of pure 2H-WS₂ it was concluded that the carbon was not incorporated in the fullerene-like nanoparticles. The source of carbon contamination is likely to originate from adsorbed organic molecules having mean thickness of 4-7 Å°. Such adsorbant signal does not seriously influence the analysis of its support - the fullerene-like material. Removal of the carbon contamination by ion sputtering was harmful to the IF structures and is not presented. Additional confirmation to that point came from local (TEM) electron energy loss measurements, which proved (due to its low sensitivity to surface contamination) that each nanoparticle consisted exclusively of W and S.

The spectra of 2H-WS₂ crystal and oxide powder, with line broadening permitted, were used as model line shapes for the deconvolution. The total error in this calculation was estimated at 1%. The high reliability of the deconvolution procedure was reaffirmed by using different pass energies. The results, expressed as I_{su} and I_{ox}, are summarized in Table I below.

The relative intensities I_{su}/I_{ox} can be converted into sulfide shell thickness (d) or number of metal chalcogenide layers (k), by considering a model type polyhedron, for which the shell and core intensities are calculated face by face:

$$I_{sul}/I_{ox} = \sum W_n I_{n,sul} / \sum W_n I_{n,ox}, \quad (1)$$

where W_n is the projection of the face area on the plane normal to the electron take-off direction (that is parallel to the substrate plane). For simplicity, a regular polyhedron was chosen for the analysis. The two I_n terms in Equation 1 are given by Briggs and Seah, (1990):

$$I_{n,sul} = \int_0^{d/\cos\Theta_n} dz I_{0,sul} \exp(-z/\lambda \cos\Theta_n) + \int_{D_n+d/\cos\Theta_n}^{D_n+2d/\cos\Theta_n} dz I_{0,sul} \exp(-z/\lambda \cos\Theta_n) \quad (2)$$

$$I_{n,ox} = \int_{d/\cos\Theta_n}^{D_n+d/\cos\Theta_n} dz I_{0,ox} \exp(-z/\lambda \cos\Theta_n)$$

The two terms in $I_{n,sul}$ stand for the contributions from the top and bottom shells of the n^{th} segment (slope). I_0 is a factor proportional to the partial density of tungsten in the compound: $I_0(sul) = I_0/3$; $I_0(ox) = I_0/3.7$. D_n is the thickness of the oxide under the face of segment n . λ is the escape depth of the photoelectrons.

The calculated values for d/λ and k , which are given in Table I below, were obtained for a polyhedron having only 6 different slopes (segments): $\Theta_n = 15^\circ n$, $n=0, \dots, N-1$. The number of slopes, $N=6$, is a representative value. In fact the numerical result becomes only weakly dependent on N for $N>3$. The value of λ was taken as ~ 2 nm (Briggs and Seah, 1990), and that of the interlayer distance ~ 0.62 nm (Wilson and Yoffe, 1968). The results of this analysis are in good agreement with the TEM observations, the main error stems from the variation in the number of WS₂ layers in the various nested polyhedra.

TABLE I:

Conversion of tungsten oxide into IF-WS₂, obtained from the deconvolution of the W (4f) peaks in a series of XPS spectra. Monochromatized Al(K α) (h ν =1486.6 eV) was used for the excitation. A monochromatized beam, (0.7 eV resolution) and a base pressure of 10⁻⁹ torr were used.

annealing time (min)	I _{ox} (%)	I _{sul} (%)	d/ λ	k
2	38	62	0.6	2
6	11	89	1.5	5
15	1.5	98.5	3.3	11
120	<0.5	>99.5		

EXAMPLE 7

Having the details of the reaction mechanism as depicted in Fig. 1 in mind, an apparatus for the synthesis of macroscopic quantities of IF particles such as WS₂, was constructed, generally referred hereinbelow as apparatus 10. The cross section of apparatus 10 is illustrated schematically in Figure 6. Thus, apparatus 10 includes a bundle of small tubes 12 arranged within a main tube 14, each of small tubes 12 serves to accommodate a preselected quantity of solid particles 16 of at least one metal material, as this term is defined hereinabove. Apparatus 10 further includes a gas flux inlet 18 in main tube 14 for introducing a forming gas and at least one chalcogen material gas. Apparatus 10 further includes heating means 20 for heating

small tubes **12** and their content. As is now understood from the above description and Examples, the preselected quantity of solid metal material particles is selected such that the solid particles are dispersed to a degree so that agglomeration and fusion of the solid particles into larger particles during heating are substantially avoided, so that the surface of the solid particles is substantially completely exposed to the chalcogen material gas.

In a preferred embodiment apparatus **10** further includes first flow control means **22** for controlling the flow of the forming gas and second flow control means **24** for controlling the flow of the chalcogen material gas.

Thus, apparatus **10** is directed at increasing the amount of the reactant and expose its entire surface to the chalcogen and forming gases. In one example a bundle of tubes **12**, seven mm in diameter each, was placed inside main tube **14** (40 mm diameter) and the oxide powder (WO_3) was dispersed in them, very loosely. Using apparatus **10**, typically, 1 g of IF- WS_2 could be obtained in a single batch, with a conversion yield of almost 100%, the major loss occurring due to evaporation of the oxide prior to the conversion with the first layer of the sulfide. This is remarkable in so far as the yield of production of carbon nested fullerenes (and nanotubes) by the arc-discharge method is a few percent, only (Kratschmer et al., 1990) 347, 354) and IF particles formed according to the prior art gas phase reaction is in the low range of 5%-20%.

With reference now to Fig. 7, presented is a preferred embodiment of an apparatus for batch-wise or continuous preparation of macroscopic quantities of inorganic fullerene-like particles of metal chalcogenides having a desired size and shape, referred to hereinbelow as apparatus **30**.

Apparatus **30** includes a chamber **32** having a lower end **34** and an upper end **36**. Chamber **32** is for accommodating solid particles **33** (e.g., a powder) of at least one metal material, say WO_3 , having the preselected size and shape. Apparatus **30** further includes a gas penetrateable cover **38** covering at least a part of lower end **34** of chamber **30**. Gas penetrateable cover **38** is for providing chamber **30** with an

inward flow of a carrier gas as indicated by arrows 40. The inward flow of a carrier gas 40 is for floating solid particles 33 in chamber 30. In a preferred embodiment the carrier gas is a forming gas including N₂ and H₂ which also provides a reducing atmosphere within chamber 30.

5 Apparatus 30 further includes a gas outlet 42 located at upper end of the chamber for sustaining the flow of gas. Apparatus 30 further includes first means 44 for introducing solid particles 33, WO₃ in the given example, into chamber 30. First means 44 may be in the form of a first inlet as shown in Figure 8, yet many other possible arrangements exist, as well known in the art. Apparatus 30 further includes
10 second means 46 for introducing at least one chalcogen material, say H₂S, into chamber 30. Second means 46 may be in the form of a second inlet 48, alternatively, cover 38 and gas flow 40 may serve as means 46. In the later case, carrier gas 40 includes also the chalcogen material, H₂S in the given example. Apparatus 30 further includes heating means 48 for heating chamber 30. In a preferred
15 embodiment chamber 32 is heated to 650 °C - 850 °C.

The operation of apparatus 30 is as follows. Solid particles 33 of transition metal material are fed into chamber 32 via first means 44 and gas flow 40 entering chamber 32 via cover 38 and leaving chamber 32 via outlet 42, ensures that solid particles 33 are floated and dispersed to a degree such that agglomeration and fusion
20 of solid particles 33 into larger particles during heating by heating means 48 are substantially avoided, so that the surface of solid particles 33 is substantially completely exposed to the chalcogen material entering chamber 32 via second means 46, as described above. As a result IF metal chalcogenide particles are formed.

It will be appreciated by one ordinarily skilled in the art that apparatus 30 is
25 suitable both for batch preparations and continuous preparation of IF particles. In the later case, solid particles 33 are continuously fed into chamber 32 via first means 44 and gas flow 40 is maintained at a level strong enough to drive the particles out of chamber 32 via outlet 42. During the time the particles are within chamber 32, e.g., 30 minutes, they are transformed into IF particles. In a preferred mode of operation,

by controlling gas flow 40, particles 33 are reacted within apparatus 30 for only few minutes (e.g., 1-2 minutes) during which a single or two layers of transition metal chalcogenide material are formed, after which the particles are collected into a dense arrangement and further reacted under otherwise similar conditions (atmosphere, 5 temperature) to obtain additional layers.

The construction and operation of apparatus 30 described hereinabove follows that of a circulating fluidized bed gas combustors, such as those described by Perry and Green (1984).

10 While the invention has been described with respect to a limited number of embodiments, it will be appreciated that many variations, modifications and other applications of the invention may be made.

REFERENCES

1. Abruna, H. D. and Bard, A. J. (1982) J. Electrochem. Soc. 129, 673.
2. Ajayan, P. M. and Iijima, S. (1993) Nature 361, 333.
3. Briggs, D. and Seah, M.P. Eds., (1990) "Practical Surface Analysis", 2nd Edition, Vol. 1, John Wiley&Sons, New York p. 233.
4. Bethune, D. S., Kiang, C. H., de Vries, M. S., Gorman, G., Savoy, R., Vazquez, J. and Beyers, R. (1993) Nature 363, 605.
- 5 5. Cartier, S.F., Chen, Z.Y., Walder, G.J., Sleppy, C.R. and Castleman, A.W. Science (1995) 260, 195.
6. Chai, Y., Guo, T., Jin, C., Haufler, R.E., Chibante, L.P.F., Fure, J., Wang, L., Alford, J.M. and Smalley, R.E. J. (1991) Phys. Chem. 95, 7564.
7. Chianelli, R. R. (1984) Catal. Rev. Sci. Eng. 26, 361.
8. Choppra, N.G., Luyken, R.J., Cherrey, K., Crespi, V.H., Cohen, M.L., Louie, 10 S.G. and Zettl, A. (1995) Science 269, 966.
9. Dagan, G. and Tomkiewicz, M. (1993) J. Phys. Chem. 97, 12651.
10. Dimigen, H. et al. (1979) Thin Solid Films 64, 221.
11. Djemal, G. et al. (1981) Sol. Energy Mater. 5, 403.
12. Ebbesen, T. W. and Ajayan, P. M. (1992) Nature 358, 220.
13. Feldman, Y., Wasserman, E., Srolovitz, D.J. and Tenne, R. (1995) Science 267, 222.
14. Greenwood, N. N. and Earnshaw, A. (1990) Chemistry of the Elements, Pergamon Press, Oxford.
15. Hershfinkel, M., Gheber, L.A., Volterra, V., Hutchison, J.L., Margulis, L. and Tenne, R.. (1994) J. Am. Chem. Soc. 116, 1914.
16. Iijima, S. (1991) Nature 354, 56.
17. Iijima, S. and Cryst, J. (1980) Growth 50, 675.
18. Iijima, S. and Ichiashi, T. (1993) Nature 363, 603.
19. Jarrold, M.J. et al. (1994) J. Phys. Chem. 98, 1810.

20. Kratschmer, W. A., Lamb, L. D., Fostiropoulos, K. and Huffman, D. R. (1990) *Nature* 347, 354.
21. Kroto, H.W. *Science* (1988) 242, 1139.
22. Kroto, H. W., O'Brien, J. R., Heath, J. R., Curl, R. F. and Smalley, R. E. (1985) *Nature* 318, 162.
23. Kung, Harold H. (1989) in "Transition Metal Oxides", Vol. 45, p. 93 Amsterdam-Oxford-New York-Tokyo.
24. Margulis, L., Salitra, G., Tenne, R. and Talianker, M. (1993) *Nature* 365, 113.
- s 25. Perry, R. H. and Green, D. Eds. (1984) *Perry's Chemical Engineers Handbook*, 6th edition, McGraw-Hill International Editions, Chemical Engineering Series, New York.
26. Porter, V.R., White, W.B. and Roy, R. (1969) *J. Solid State Chem.* 1, 359.
27. Robertson, D. H., Brenner, D. W. and White, C. T. (1992) *J. Phys. Chem.* 96, 6133.
28. Rosenberg, I., Brock, J. R. and Heller, A (1992) *J. Phys. Chem.* 96, 3423.
29. Rouxel, J. and Brec, R. A. (1986) *Rev. Mater. Sci.* 16, 137.
30. A. Ruoff, R.S., Lorents, D.C., Chan, B., Malhorta, R. and Subramoney, S. 10 *Science* (1993) 259, 346.
31. Schmidt, E., Sourisseau, C., Meunier, G. and Levasseur, A. (1994) *Thin Solid Films* 245, 34.
32. Schmidt, E., Weill, F., Meunier, G. and Levasseur, (1995) *A. Thin Solid Films* 260, 21.
33. Seraphin, S., Zhou, D., Jiao, J., Withers, J.C. and Lotfy, R. (1993) *Nature* 362, 503.
34. Srolovitz, D.J., Safran, S.A., Homyonfer, M. and Tenne, R. (1995) *Phys. Rev. Lett.* 74, 1778.
35. Stephane, O., Ajayan, P.M., Colliex, C., Redlich, Ph., Lambert, J.M., Bernier, P. and Lefin, P. (1994) *Science* 266, 1683.

36. Takata, M., Umeda, B., Nishibori, E., Sakata, M., Saito, Y., Ohno, M. and Shinohara, H. (1995) *Nature* 377, 46.
37. Tenne, R., Margulis, L., Genut, M. and Hodes, G. (1992) *Nature* 360, 444.
38. Tributsch, H. (1982) in *Structure and Bonding*, Springer Verlag, Berlin, 49, 127.
39. Ugarte, D. (1992) *Nature* 359, 707.
40. Wells, A. F. (1993) *Structural Inorganic Chemistry*, 5th edition, Oxford Science Publications.
41. Weng-Sieh, Z., Cherrey, K., Chopra, N.G., Blase, X., Miyamoto, Y., Rubio, A., Cohen, M.L., Louie, S.G., Zettl, A. and Gronsky, R. (1994) *Phys. Rev. B* 51, 11229. 5.
42. Wilson, J. A. and Yoffe, A. D. (1968) *Adv. Phys.* 18, 193.

CLAIMS:

1. A solid-gas method for the bulk synthesis of inorganic fullerene-like (hereinafter IF) structures of metal chalcogenides from a solid non-volatile metal material precursor, said IF structures having a desired size and shape being predetermined by the size and shape of the said metal material precursor, wherein said metal is selected from In, Ga, Sn and a transition metal selected from Mo, W, V, Zr, Hf, Pt, Re, Nb, Ta, Ti, Cr and Ru., the method comprising the steps of:

(a) dispersing in a reactor solid nanoparticles of at least one non-volatile metal material having the preselected size and shape, said dispersion being such that, upon heating, agglomeration and fusion of said solid nanoparticles into larger particles are substantially avoided, so that the top surface of said solid particles is substantially completely exposed to a gaseous atmosphere;

(b) heating said dispersed solid particles of said non-volatile metal material in a reducing gaseous atmosphere containing at least one chalcogen material for a time and a temperature sufficient to allow the reaction of the top surface of said metal material nanoparticles with said chalcogen material gas, said IF nanoparticles having at least one completely closed monomolecular metal chalcogenide layer encaging said metal material particles; and

(c) recovering the thus obtained macroscopic quantities of the IF-metal chalcogenide structures of the desired size and shape.

2. A method according to claim 1 wherein in step (a) heating is carried out a temperature within the range of 650-850 °C for a time shorter than 60 seconds to produce IF structures with one layer encaging said metal material, and for 1-20 min to produce IF structures with 2-5 layers encaging said metal material.

3. A method according to claim 1 or 2, which comprises further heating the IF particles of step (a) at the same temperature in said reducing gaseous atmosphere

containing said at least one chalcogen material gas for a time sufficient to allow said metal material and said chalcogen material gas to further react through a slow diffusion controlled reaction, wherein the metal material core is progressively converted into a metal chalcogenide nanoparticle with an empty core, and nested IF-metal chalcogenide structures are thus obtained and recovered.

4. A method according to claim 3 wherein the reaction mixture is further heated at 650-850 °C for 20-120 min to produce multilayered IF structures.

5. A method according to any one of claims 1 to 4, wherein the metal is a transition metal selected from Mo, W, V, Zr, Hf, Pt, Re, Nb, Ta, Ti, Cr and Ru..

6. A method according to any one of claims 1 to 5, wherein said at least one non-volatile metal material is selected from the group consisting of a metal, a compound containing a metal, a mixture of metals, a mixture of compounds containing a metal and a mixture of a metal and a compound containing a metal.

7. A method according to claim 6, wherein said non-volatile metal material is selected from the group consisting of a metal, a mixture of metals, a metal alloy, a metal oxide, and a metal carbide.

8. A method according to claim 7, wherein said metal material is a metal oxide selected from a tungsten oxide selected from WO_3 , $\text{W}_{20}\text{O}_{58}$, and $\text{W}_{18}\text{O}_{49}$; ZrO_2 , HfO_2 , PtO_2 , In_2O_3 , Ga_2O_3 , Nb_2O_5 , Ta_2O_3 , ReO_3 , TiO_2 , SnO_2 , and RuO_2 .

9. A method according to any one of claims 1 to 8, wherein said at least one chalcogen material is selected from the group consisting of a chalcogen, a compound containing a chalcogen, a mixture of chalcogens, a mixture of compounds containing a chalcogen and a mixture of a chalcogen and a compound containing a chalcogen.

10. A method according to claim 9, wherein said chalcogen material is selected from the group consisting of H_2S , H_2Se , H_2Te and mixtures thereof.
11. A method according to any one of claims 1 to 10, wherein said desired shape of said IF-metal chalcogenide nanoparticles is selected from the group consisting of spheres, sphere-like, and nanotubes.
12. A method according to Claim 11, wherein said spheres, sphere-like, and nanotubes of said IF-metal chalcogenide nanoparticles have 1-5 layers of the metal chalcogenide encaging a core of the metal material precursor.
13. A method according to Claim 11, wherein said spheres, sphere-like, and nanotubes of said IF-metal chalcogenide nanoparticles are multilayered structures with a hollow core.
14. A method according to claim 1 wherein the metal material is WO_3 and the chalcogen material is H_2S gas, wherein the solid WO_3 nanoparticles are first dispersed on the floor of the reactor to avoid agglomeration and fusion of the heated nanoparticles, the dispersed nanoparticles of WO_3 are reacted at a temperature in the range of 650-850°C with a mixture of H_2S gas with a forming gas (95% N_2 /5% H_2), whereby the WO_3 is reduced to WO_{3-x} and gradually converted to WS_2 , and the reaction products are collected on a substrate and progressively converted into the desired nested IF- WS_2 polyhedra.
15. Apparatus for preparing macroscopic quantities of inorganic fullerene-like nanoparticles of metal chalcogenides having a desired size and shape according to the method of any one of Claims 1-14, the apparatus comprising:

(a) a bundle of small tubes arranged within a main tube, each of said small tubes being for accommodating a preselected quantity of solid nanoparticles of at least one non-volatile metal material having the preselected size and shape;

(b) a gas flux inlet in said main tube for introducing a forming gas and at least one chalcogen material gas; and

(c) heating means for heating said small tubes;

said preselected quantity of the non-volatile metal material being selected such that said solid nanoparticles are dispersed to a degree such that agglomeration and fusion of said solid nanoparticles into larger particles during said heating are substantially avoided, while the surface of said nanoparticles is substantially completely exposed to said chalcogen material gas.

16. An apparatus according to claim 15, further comprising:

(d) first flow control means for controlling the flow of forming gas; and

(e) second flow control means for controlling the flow of chalcogen material gas.

17. Apparatus for preparing macroscopic quantities of inorganic fullerene-like nanoparticles of metal chalcogenides having a desired size and shape according to the method of any one of Claims 1-14, the apparatus comprising:

(a) a chamber having a lower end and an upper end, said chamber being for accommodating solid nanoparticles of at least one non-volatile metal material having a preselected size and shape;

(b) a gas penetrateable cover covering said lower end of said chamber, said gas penetrateable cover being for providing said chamber with an inward flow of carrier gas for floating said solid particles in said chamber;

(c) a gas outlet located at said upper end of said chamber for sustaining said flow of gas;

- (d) first means for introducing said solid particles into said chamber;
- (e) second means for introducing at least one chalcogen material into said chamber; and
- (f) heating means for heating said chamber;

said flow of gas being selected such that said solid nanoparticles of the non-volatile metal material are dispersed to a degree such that agglomeration and fusion of said solid particles into larger particles during said heating are substantially avoided, while the surface of said solid particles is substantially completely exposed to said chalcogen material gas.

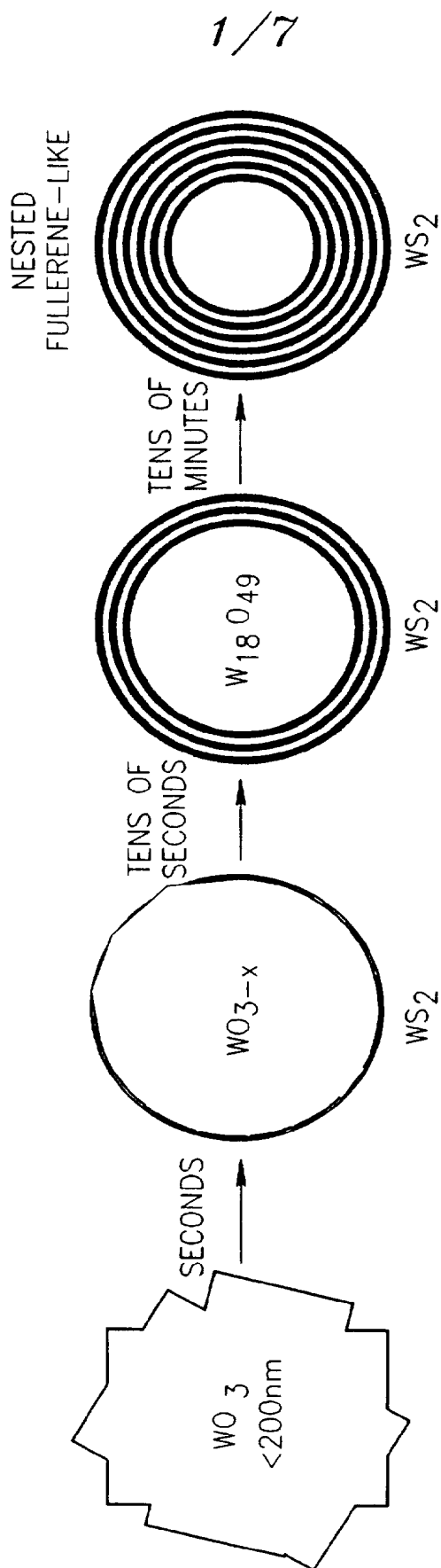


FIG.1

FIG.2A

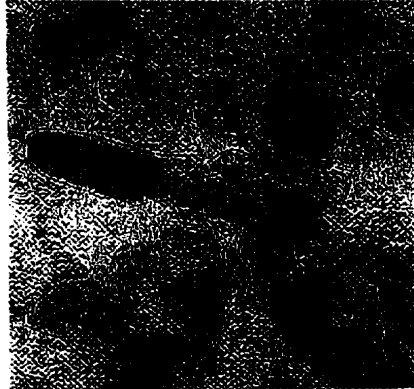
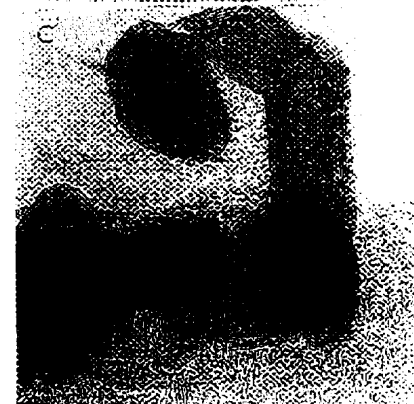


FIG.2B



FIG.2C



3/7

FIG.3A

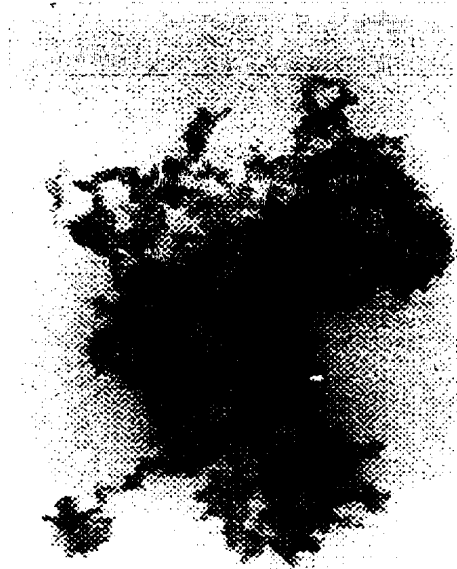


FIG.3B



FIG.3C

FIG.3D

4/7

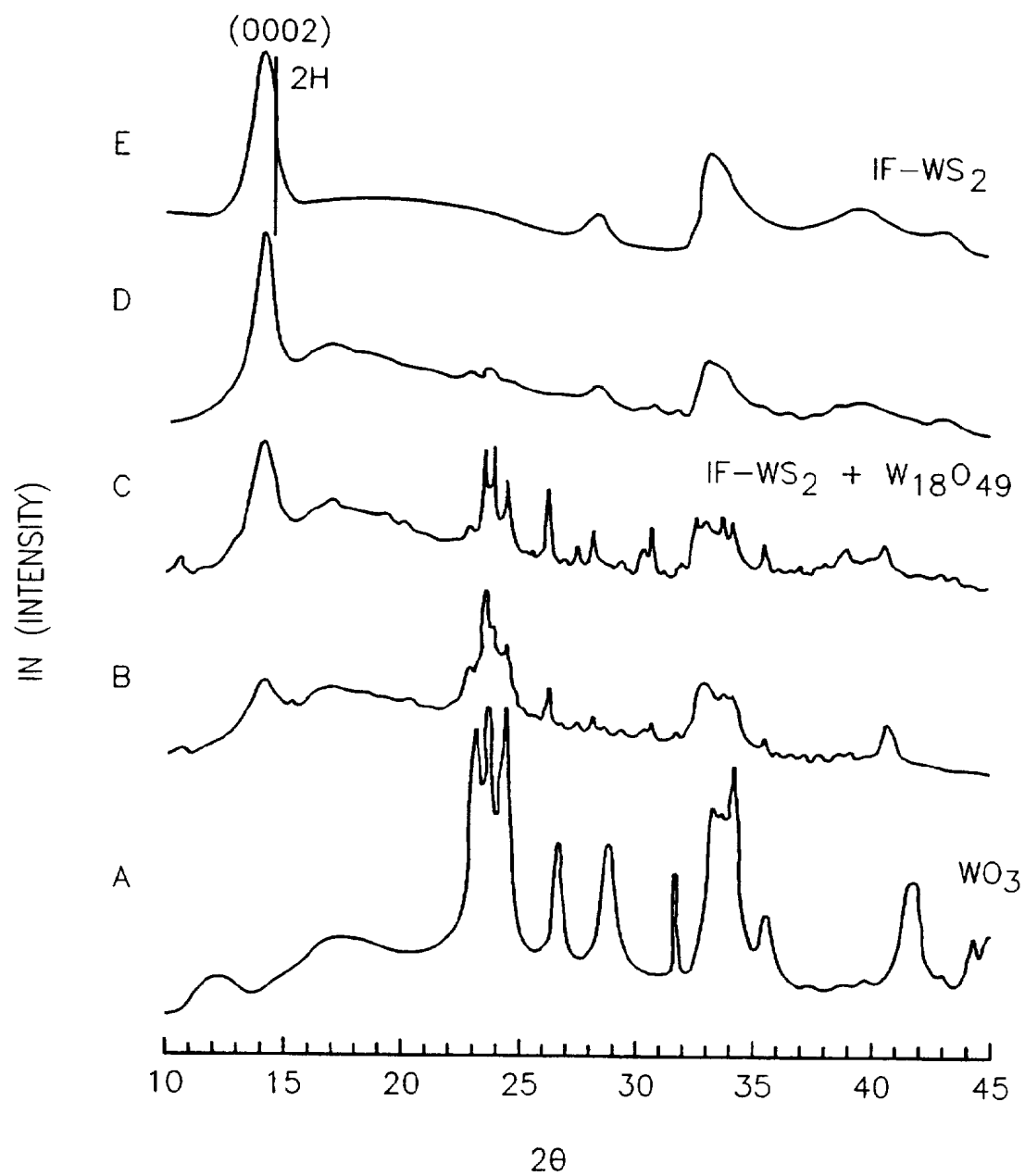


FIG.4

5/7

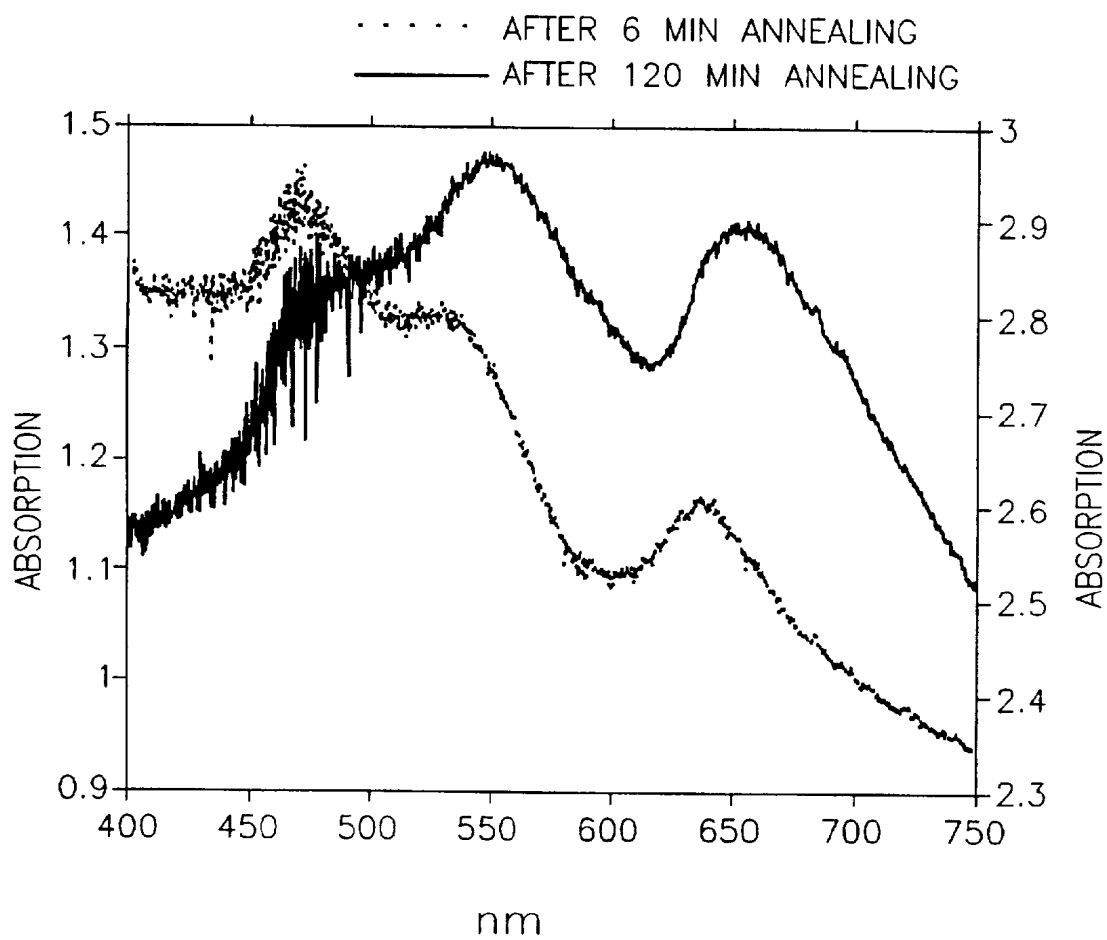


FIG.5

6/7

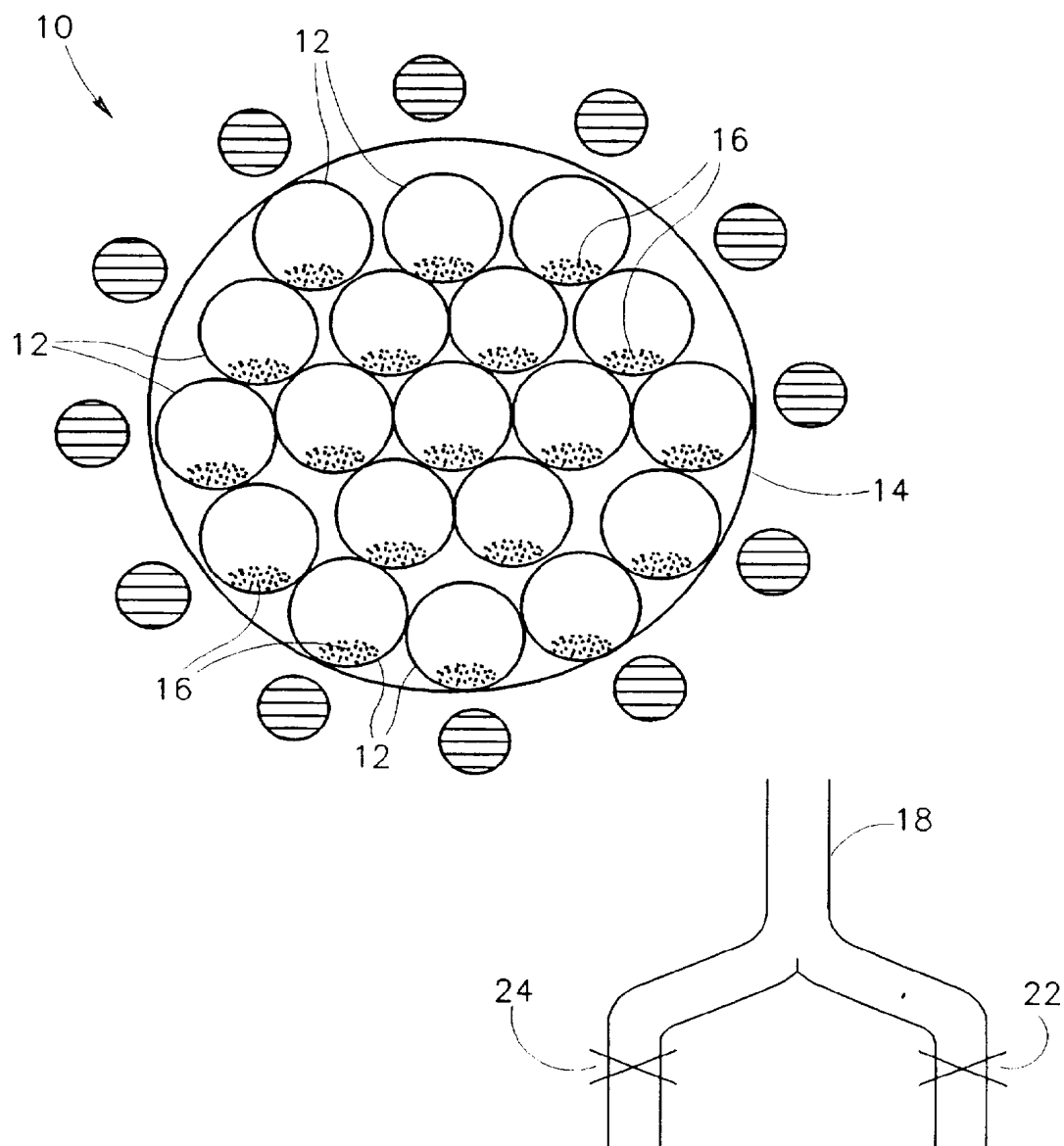


FIG. 6

7/7

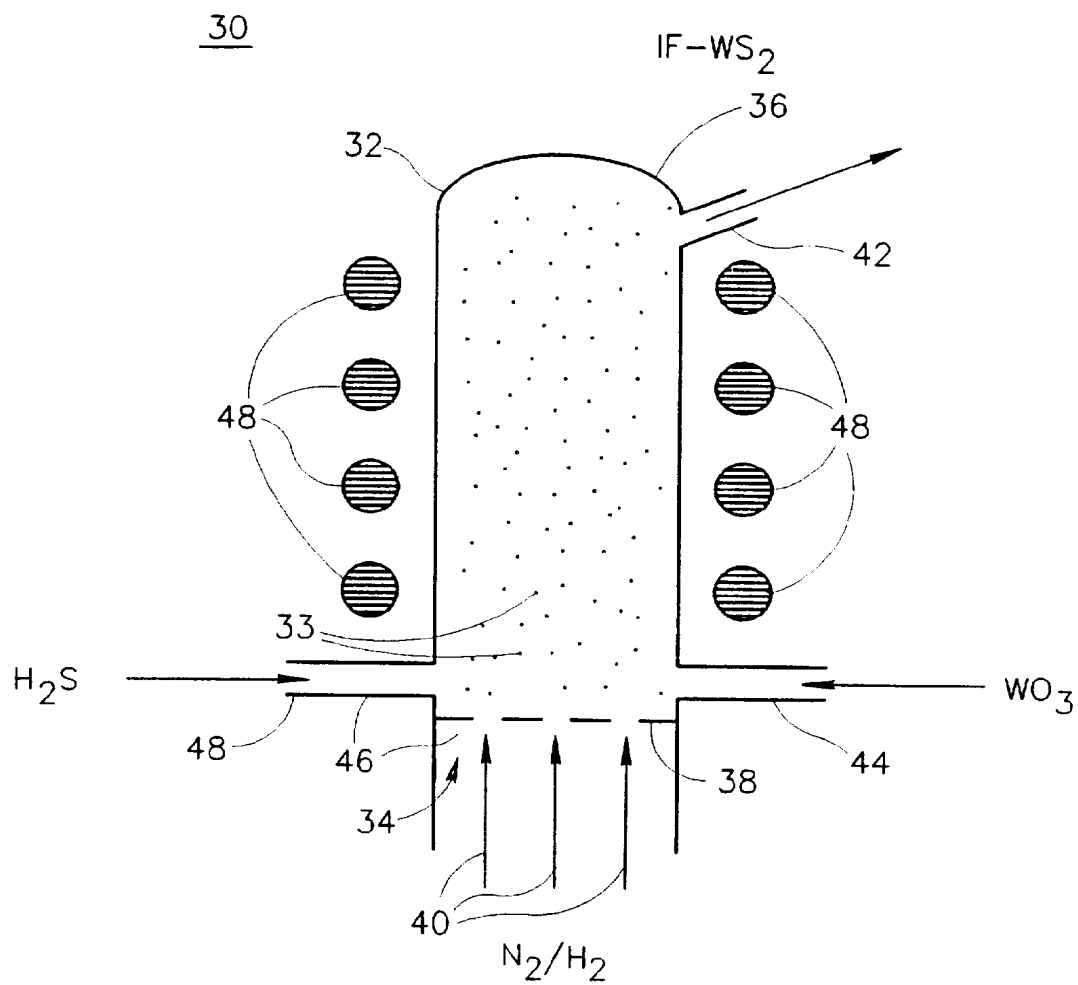


FIG.7

INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/IL 97/00165

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01G1/12 C01G41/00 C01B17/20 C01B19/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01G C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>PROCEEDINGS OF THE INTERNATIONAL WINTERSCHOOL ON ELECTRONIC PROPERTIES OF NOVEL MATERIALS. FULLERENES AND FULLERENE NANOSTRUCTURES, KIRCHBERG, TYROL, AUSTRIA, 2 - 9 March 1996, pages 445-453, XP002040987</p> <p>FREY G. L. ET AL.: "Inorganic fullerene-like MS2 (M=Mo, W) structures: synthesis, reaction mechanism and characterization" see abstract</p> <p>see page 446, 'Experimental', paragraph 2</p> <p>see page 448, paragraph 3</p> <p style="text-align: center;">---</p> <p style="text-align: center;">-/-</p>	1,5-14

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

17 September 1997

Date of mailing of the international search report

3 0. 09. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Rigondaud, B

INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/IL 97/00165

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 118, no. 23, 12 June 1996, DC US, pages 5362-5367, XP002040984 FELDMAN Y. & AL.: "Bulk synthesis of inorganic fullerene-like MS ₂ (M = Mo, W) from the respective trioxides and the reaction mechanism" see the whole document ---	1,3,5-15
A	SCIENCE, vol. 267, 13 January 1995, US, pages 222-225, XP002040985 FELDMAN Y. E. & AL.: "High-rate, gas-phase growth of MoS ₂ nested inorganic fullerenes and nanotubes" cited in the application see the whole document ---	1,15,17
A	EP 0 580 019 A (YEDA RESEARCH AND DEVELOPMENT COMPANY, LTD) 26 January 1994 cited in the application see claims 1,2,4 see example 4 ---	1
A	COMPTES RENDUS HEBDOMADAIRES DES SEANCES DE L'ACADEMIE DES SCIENCES, SERIE C: SCIENCES CHIMIQUES, vol. 268, no. 25, 23 June 1969, MONTREUIL FR, pages 2142-2145, XP002040986 LE BOËTE F. & AL.: "Préparation du disulfure de tungstène par sulfuration du trioxyde sous faible pression de sulfure d'hydrogène. Aspect cinétique et morphologique de cette réaction" ---	
A	US 3 313 601 A (ORRIN F. MARVIN) 11 April 1967 see claim 9 -----	1

INTERNATIONAL SEARCH REPORT

information on patent family members

Intern. Application No

PCT/IL 97/00165

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 580019 A	26-01-94	JP 7069782 A	14-03-95
US 3313601 A	11-04-67	NONE	